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DETERMINATION OF THE IMPREGNANT CONCENTRATIONS ON ASC TYPE CHARCOAL. A MAGNETIC SUSCEPTIBILITY STUDY (U)

by

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ABSTRACT

A non-destructive test has been developed to monitor the impregnants in charcoal. A study of some commercially-produced and custom-made ASC-whetlerites indicates significant increases in the measured magnetic susceptibility from that of the base charcoal. Correlations between the measured susceptibilities and the concentrations of copper and chromium by a linear mathematical model are established with reasonably good fit for the custom-made charcoals. It is concluded that the magnetic susceptibility data would be best utilized as a qualitative tool for the assessment of metal impregnants on charcoal, rather than for precise quantitative analyses. Some preliminary data on the magnetic susceptibilities of ASC-whetlerites co-impregnated with TEDA are also presented. Magnetic susceptibilities measured on the same charcoal samples by commercial instruments indicate that although they show similar trends as the Gouy balance, these instruments are subject to too much variation to be of any qualitative and/or quantitative use for ASC charcoals.

RÉSUMÉ

Un test non destructif a été développé dans le but d'évaluer la quantité de solides d'imprégnation utilisés dans cértains types de charbons actives. Une étude de faisabilté effectuée sur des charbons activés ASC-whetlerite de sources commerciales ou préparés en laboratoire a permis de détecter une augmentation significative de la susceptibilité magnétique de ceux-ci par rapport au charbon activé de base. Une corrélation entre le degré de susceptibilité et la concentration en cuivre et en chromium fut effectuée et une régression linéaire a donné un bon degré d'ajustement des données dans le cas des charbons activés préparés en laboratoire. On conclu que la susceptibilité magnétique peut être utilisée comme outil qualitatif pour l'évaluation des solides d'imprégnation du charbon activé. Le degré de précision obtenu n'est cependant pas assez élevé pour faire une analyse quantitative. Des données préliminaires de la susceptibilité magnétique des charbons activés ASC-whetlerite co-imprégnés de TEDA sont aussi présentées. Des mesures de la susceptibilité magnétique de ces mêmes échantillons effectuées à l'aide d'appereils commerciaux a permis de déterminer que bien que les résultats démontrent la même tendance générale que pour la balance de Gouy; les variations sont trop grandes pour permettre une analyse qualitative ou quantitative valable.

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1.0 INTRODUCTION

It is well documented that the capacity to remove toxic gases by activated charcoal is enhanced by the impregnation of the charcoal with inorganic and/or organic chemicals (1). This process of impregnation is better known as whetlerization, and the impregnated charcoal is therefore called whetlerite. Whetlerite charcoals remove toxic gases by physical adsorption of organic molecules and by chemical reaction with small molecules such as hydrogen cyanide, cyanogen chloride, phosgene and arsine. The adsorptive and catalytic properties of whetlerite are dependent upon the nature of the pores in the charcoal and upon the chemical materials other than carbon which are present in the whetlerite. ASC whetlerite (a copper-silver-hexavalent chromium impregnated charcoal) is the current choice for military air-filters and respirators. This choice, over other inorganic impregnants, is based on the better protection afforded by ASC-whetlerite against war gases such as cyanogen chloride (CK), phosgene (CG), and hydrogen cyanide (AC).

It is well established that the capacity of ASC whetlerite for cyanogen chloride is strongly dependent on the moisture content of the charcoal (2). Also, it is a common experience that ASC whetlerite which has been stored for some time, does not reach its original CK capacity even after the desorption of water. This phenomenon is called aging. The aging of ASC-whetlerite has been studied mainly by x-ray techniques (3-5,7), which only revealed the microstructures of the crystallites formed by the impregnants on the surfaces of the charcoal. The conclusion from these studies is that aging arises from the changes in the crystalline form and location of the metals and the formation of cupric oxide crystallites on the surface of the charcoal. It is believed that this transformation is responsible for reducing the capacity for CK adsorption. It is also believed that Cr(VI) used in the ASC whetlerite is reduced to Cr_2O, upon aging.

In the course of the charcoal research and development carried out in this laboratory, it has become necessary to monitor the impregnant concentrations. Although the existing "wet methods" are sufficiently accurate and precise to perform all the analyses, they are labor intensive and involve the destruction of the impregnated charcoal to extract all the impregnants. It is the intention of this project to review and assess a simple non-destructive method for the analysis of copper and chromium in charcoal based on magnetic properties. Two potential applications of a non-destructive analytical technique for ASC charcoal could be a residual life indicator for large collective protection filters or an on-line quality assurance operation on a filter assembly line. Other, more elaborate non-destructive methods include the use of x-ray techniques (6,7) for charcoal analysis. This report contains the design and calibration of

a Gouy balance for the purpose of magnetic susceptibility measurements of charcoal. Some preliminary results on charcoal samples are also presented.

1.1 SURVEY OF MAGNETIC STUDIES ON CHARCOAL

During the 1940's and 1950's, Clément Courty published a series of reports on the adsorption on charcoal studied by magnetic measurements (8). Most of these studies concerned the measurement of the magnetic susceptibility of adsorbates such as oxygen, air, water, carbon disulfide and chloropicrin etc., before and after adsorption on the diamagnetic charcoal prepared from coconut shell. However, the conclusions drawn from these magnetic measurements were neither clear nor definite.

The other reported use of magnetic susceptibility measurements for charcoal studies was the monitoring of the state of the impregnants by means of a Gouy or a Faraday balance (9). This procedure did not require the drastic treatments (refluxing, etc.) usually involved in the "wet chemistry" analytical procedures. The large differences between the magnetic susceptibilities of compounds of copper and compounds of chromium suggested that the valence state of the impregnants might be determined by this means.

However, the above work appears to have been halted around 1945, and it is the intent of this report to further explore the usefulness of magnetic susceptibility measurements using a Gouy balance in the elucidation of the concentration and the state of the impregnants in ASC charcoal.

2.0 THEORY

Magnetic susceptibility is the response of a material to the presence of a magnetic field. This technique, as it is practiced today, is a formidable research tool that provides chemical and physical information on systems being studied by all branches of science. This statement is substantiated by the number of magnetic investigations on chemical compounds which have increased over the years. The voluminous tabulation by Konig and Konig (10) further attests to this fact. Many general reviews on magnetic susceptibility are available that include various experimental

techniques (11-15), methods of theoretical analysis (11, 16-18), and surveys of literature reports (19-23). Some recent advances in instrumentation, such as the vibrating sample magnetometer (24), the alternative force magnetometer (25), and the superconducting susceptometer (26) will not be discussed here because of their irrelevancy. The following section will discuss briefly the theoretical treatment of magnetic susceptibility.

2.1 MAGNETIC RESPONSE

It is well known that some substances are attracted to a magnetic field while others are repelled from it. When a substance is placed inside a magnetic field $\bar{H}$, the density of the magnetic lines of force within the substance (magnetic induction, $\bar{B}$) may be expressed as:

$$\bar{B} = \bar{H} + 4\pi\bar{M} \qquad [1]$$

where $\bar{M}$ is the magnetization.

A substance is magnetically isotropic when both the magnitude and the direction of $\bar{M}$ do not depend on the orientation. The susceptibility of a material to the presence of a magnetic field χ is often assigned as the scalar ratio of the magnetization and the magnitude of the magnetic field,

$$\chi = M/H \qquad [2]$$

Equation [2] should be more appropriately written as,

$$\bar{M} = \chi \cdot \bar{H} \qquad [3]$$

this is because χ, $\bar{M}$ and $\bar{H}$ are not necessarily coincident, and secondly, χ, the magnetic susceptibility is a second-rank tensor. In a suitable coordinate system, χ could be diagonalized with χ_1, χ_2, χ_3 as the principal susceptibilities. In the special case of a magnetically isotropic specimen, then $\chi_1 = \chi_2 = \chi_3$, and equation [2] applies. (Of course, this also implies that $\bar{M}$ is coincident with both $\bar{H}$ and $\bar{B}$.)

Another special case in which [2] applies is when an anisotropic specimen is oriented in such a way that the magnetic field is coincident with the principal susceptibility axes.

The sign of the magnetic susceptibility usually depends on whether the ground-state electrons in a particular molecule are paired or unpaired. However, the ability to accomodate unpaired electrons in low-lying yet thermally unpopulated excited states may contribute substantially to the magnetic susceptibility. In such cases, it is possible to observe a net positive magnetic susceptibility, even when the ground state is a spin paired singlet. In the absence of this second-order paramagnetism, most materials can be divided into two categories: diamagnetic, and paramagnetic. Diamagnetism is characterized by electron spins paired in the molecule and the repulsion of the substance away from the region of higher field. In a diamagnetic material, the magnetic induction $\bar{B}$ is smaller than the magnetic field $\bar{H}$, and the magnetic susceptibility is negative. Paramagnetism is characterized by unpaired electron spins in the molecule and an attraction of the sample to the region of high magnetic field. In this case, the magnetic induction $\bar{B}$ is larger than the static magnetic field and the magnetic susceptibility is positive. Ferromagnetism and antiferromagnetism are considered subcategories under paramagnetism, and they refer to the special orientation of the electron spins inside a magnetic field.

2.2 DIAMAGNETISM AND PARAMAGNETISM

Diamagnetism is fundamental to all chemical compounds and contributes a small (typically 10^{-6} to 10^{-7} emu-g^{-1}) negative component to the magnetic susceptibility of a material. Diamagnetism is independent of temperature and is generated by electrons moving in a closed orbit. Pascal (27) proposed an empirical equation for the representation of diamagnetic susceptibility as

$$\chi_{dia} = \lambda + \sum_i n_i \chi_i \qquad [4]$$

where n_i is the number of atoms of each type, χ_i is the contribution to the susceptibility of each of the constituent atoms and λ is a constitutive correction that depends on the type of bonds in the molecule. For most measurements of interest to inorganic magnetochemists, diamagnetic corrections are usually much smaller than the paramagnetic ones, which are of prime interest. It should be noted that this derivation of Pascal's constant is empirical, and is the result of a judicious mathematical juggling of numbers.

On the other hand, paramagnetism is generated by the tendency of magnetic angular momentum to orient itself in a magnetic field. At room temperature, paramagnetism is usually one to three orders of magnitude larger than diamagnetism (ca. 10^{-4} to 10^{-6} emu-g^{-1}) and results in a positive contribution to the bulk magnetic susceptibility. An empirical formula for the magnetic susceptibility of a paramagnetic sample was developed by Curie (28):

$$\chi = C/T \qquad [5]$$

where T is the temperature and C is the Curie's constant, which, for spin-only magnetic susceptibility is given by

$$C = \frac{Ng^2 \mu_B^2 S(S+1)}{3k} \qquad [6]$$

where N = Avogadro's number
g = Lande's splitting factor ≈ 2.0
μ_B = Bohr's magneton
S = spin angular momentum
k = Boltzmann's constant

A weak magnetic interaction between neighbouring spins in a crystalline material may be approximated as a perturbation to equation [5]. The functional dependence of this interaction may then be described by replacing the temperature parameter in eqn. [5] with a (T-θ) term, giving the Curie-Weiss law:

$$\chi_M = \frac{Ng^2 \mu_B^2 S(S+1)}{3k\ (T-\theta)} \qquad [7]$$

where χ_M is the molar magnetic susceptibility with units of emu-$mole^{-1}$ and the Weiss constant θ has the units of Kelvin. A plot of the inverse of the magnetic susceptibility for a system that obeys the Curie-Weiss law yields a straight line. The value of g and Curie's constant could be calculated from the slope of the line, while the sign and magnitude of the Weiss constant could be extrapolated from the intercept. A positive θ may be caused by ferromagnetic spin interaction, while a negative value may be caused by antiferromagnetic spin states.

2.3 INFORMATION OBTAINABLE FROM MAGNETIC MEASUREMENTS

Using any standard method, it is possible to determine whether the magnetic susceptibility of a material is dependent on (a) temperature; (b) the field strength; or (c) both of these factors. This yields qualitative information as to whether the material is dia-, para-, or ferromagnetic.

Thermomagnetic analysis (13,29) yields valuable information on the particle size distribution and activity of ferromagnetic catalysts. Measurements of magnetization give composition of alloys, the degree of precipitation of a metal in its alloy, the carbon content in steel, and so on. The susceptibility of a paramagnetic system that includes solid and gaseous mixtures, solutions and colloids and dispersed media, such as glass, yields the concentration of a transition metal, rare earth, or a paramagnetic gas involved in any of these systems (11).

Detection and determination of the concentration of free radicals from organometals undergoing dissociation can also be monitored by dia- or paramagnetic measurements. Examples of all of these measurements may be seen in the open literature (11, 13-15).

2.4 PRINCIPLES OF MAGNETIC MEASUREMENTS

Magnetic susceptibilities are generally measured by the so-called uniform field or nonuniform field methods. Since a Gouy balance was used in this study, only the principles of the uniform field method will be discussed.

In this method, a long cylindrical sample is suspended vertically between the poles of a magnet such that one end lies in a region of strong magnetic field, while the other end lies in a region of negligible field (i.e. relatively far away from the centre of the pole faces). The sample would then experience an orienting effect in the magnetic field depending on its anisotropy. This effect will be directly proportional to a product of its volume susceptibility, K (= $\chi.\rho$, where ρ is the density of the material), its volume, V, and the applied field, H. The body will experience a linear displacing force, F, if the field is made nonuniform with a gradient $\partial H/\partial z$ in the z-direction (i.e. vertically), which is given by

$$F = K.V.H.\ \partial H/\partial z \qquad [8]$$

Integrating equation [8] over all layers between the limits of maximum field H, and of negligible field (H = 0) gives,

$$F = \tfrac{1}{2} K.H^2.A \qquad [9]$$

where A is the cross-sectional area of the sample. This equation tacitly assumes that the atmosphere surrounding the sample has a negligible susceptibility, and that the field at one end of the tube is negligible in comparison to that at the other. If these conditions are not fulfilled so that the atmosphere has a susceptibility of K_o and the field at the other end is H_o, then the equation for F becomes

$$F = \tfrac{1}{2}(K - K_o)(H^2 - H_o^2)\, A \qquad [10]$$

The necessity of having a uniform field between the pole gap rises from practical considerations. If the field is not uniform, the sample will experience a horizontal force, and it may tend to move toward one of the pole faces and thus require an exact measurement of the vertical force. Suitable monitoring of the vertical force F (by a semi-microbalance) and the applied magnetic field (by a gaussmeter) will then yield the magnetic susceptibility.

3.0 EXPERIMENTAL

3.1 SET-UP

Figure 1 illustrates the experimental set-up of a custom-built Gouy balance. The semi-micro balance used is a Sartorius model 2004-MP6, capable of weighing accurately to ± 0.00001 gm. Some holes were drilled in the balance pan to offset the extra weight hanging from it, so that the balance could always be tared back to zero. A smaller hole was drilled in the center of the pan to allow the passage of a thin wire from which the sample cylinder was attached. For the same purpose, a hole has been drilled in the base plate of the balance. The "wire" was actually a 29 cm-long piece of a Hewlett-Packard 530 μ fused silica capillary column. This choice is made based on the inertness, flexibility and the inherent straightness of the fused silica column. The silica column was attached to

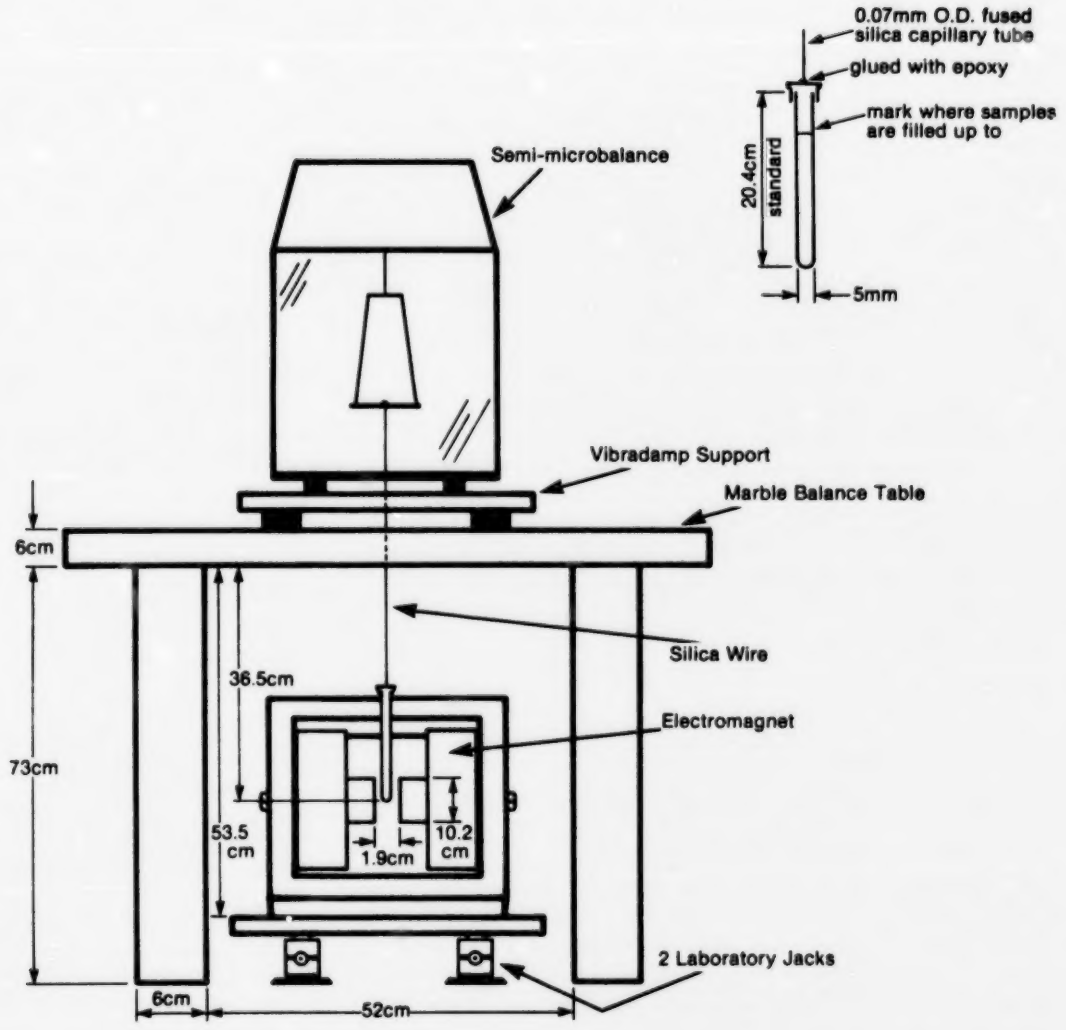


Figure 1: Schematic of the Gouy balance set-up.

the pan with epoxy. The bottom end of the silica column was glued (also with epoxy) to a cap fitted to a 5 mm o.d. nmr tube. The 5 mm o.d. nmr tubes used were of ultraprecision grade from Varian Associates. They are 20.37 cm in length with an i.d. of 4.22 mm. This simple set-up allows easy sample changing and handling. The powdered sample to be analyzed could be packed into the nmr tube and then fitted to the cap. The fused silica column is very flexible, and therefore allows repeated changing of samples.

The balance was placed on a vibradamp support and then on a marble balance table, both supplied by Fisher Scientific Co. This minimized vibrations from the environment. The nmr tube (sample tube) was suspended vertically between the two pole faces of an electromagnet, with the bottom of the sample tube leveled against the center of the pole faces. The 4-inch electromagnet and the power supply were both from Alpha Scientific Co. The electromagnet had a pole gap of 2 cm, and was supported by two laboratory jacks to maintain the condition that the bottom of the sample tube is always at the centre of the pole face. The spaces between the balance and the vibradamp support and between the support and the marble table were sealed with tape to stop draft. The underside perimeter of the balance table was covered with hard cardboard paper and sealed at all edges to minimize air draft. The front of this cardboard cage had a "door" made of transparent plastic for easy access to the sample tube and magnet, and so that any mis-alignment of the sample tube during measurement could be observed.

3.2 EXPERIMENTAL AND REAGENTS

All magnetic susceptibility measurements were performed at ambient temperature (24 ± 1°C).

All the 5 mm o.d. nmr tubes had a mark engraved on the side of the tubes at about 14.76 cm from the bottom, so that all liquid or solid chemicals were only filled to this mark. The volumes of the tubes up to this mark were calibrated with water at ambient temperature. These volumes were found to average about 2.04 ml.

All chemicals used in the magnetic measurements were purified before use. The benzene (from Fisher Scientific Co.) was distilled over sodium and stored over molecular sieve type 3A. The benzene was also saturated with air before use. The water used was distilled water deionized with an ion resin exchanger. The water was also saturated with air. Both references (water and benzene), when saturated with air, have mass magnetic suceptibilities of -0.720×10^{-6} emu-g^{-1} and -0.702×10^{-6} emu-g^{-1} respectively (11).

The solid samples, such as chromium nitrate nanohydrate (from Aldrich Chemical Co.), copper sulfate pentahydrate (from Fisher Scientific Co.) and mercury tetracyanatocobaltate, ($HgCo(NCS)_4$) (30) were all used fresh from the bottle.

The liquid samples were loaded into the nmr tubes with disposable pipets. The solid samples to be used in magnetic susceptibility measurements were first ground to fine powders with average diameters less than 0.2 mm (65 mesh) by a Moulinex grinder. The grinding was performed to our satisfaction that no additional impurities were introduced in the process. The charcoal samples used in this report were dried in a compressed air oven at 60°C for several days before magnetic measurements were made. The solid was then loaded into the nmr tube in small batches (of about 5 mm in height every time), and was then tapped and vibrated to pack tightly before the next batch was added.

The nmr tubes were weighed before and after the introduction of the sample, so that the net weight and the packing density of the sample could be calculated.

In view of the general difficulty in setting up the apparatus, the use of commercial instruments was evaluated. Some preliminary data and recommendations are included in Appendix A.

3.3 CALIBRATION AND CALCULATION

The experimental set-up for the calibration of the electromagnet is summarized in Figure 2. The magnetic field was monitored by a gaussmeter while the applied voltage across the magnet was varied. A plot of the variation of the magnetic field vs applied voltage is shown in Figure 3. Normally, the magnetic field is calibrated against the applied current. Since each data point in this calibration was taken every 10 minutes, and each measurement lasted about 1-2 seconds, it is assumed that there is no appreciable magnet heat-up and voltage fluctuations.

For calculation of magnetic susceptibility, the following symbols were used: W = weight, d = density, K = volume susceptibility, χ = gram susceptibility, ΔW = change in weight on applying the magnetic field, and V = actual volume up to the mark ($=W_r/d_r$). The subscripts r,s, and t correspond to the reference, the sample, and the tube.

For measurements at a fixed field,

$$\Delta W_r = W_{(r+t)} - W_t \qquad [11]$$

$$\Delta W_s = W_{(t+s)} - W_t \qquad [12]$$

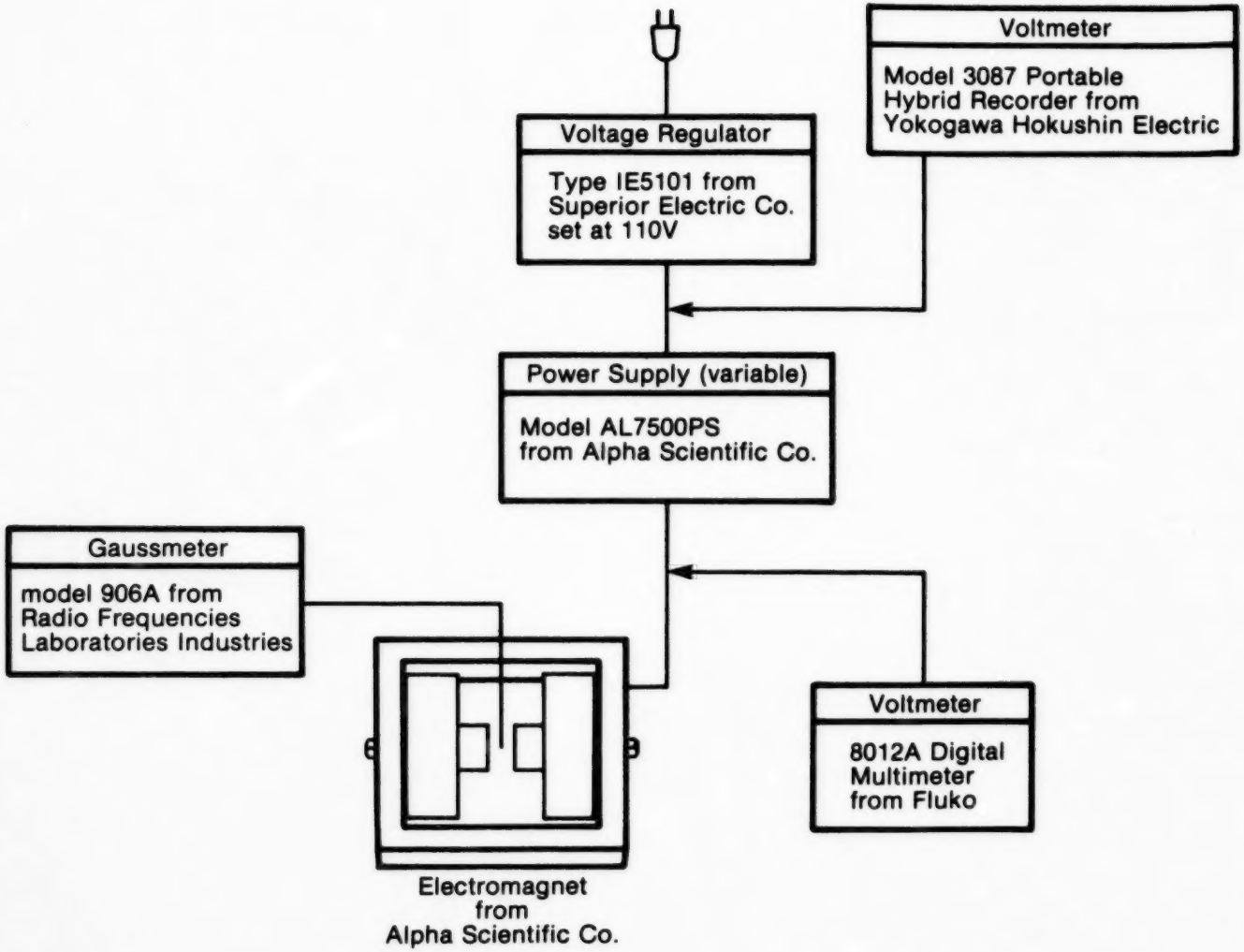


Figure 2: Schematic of the Calibration set-up for the Gouy balance.

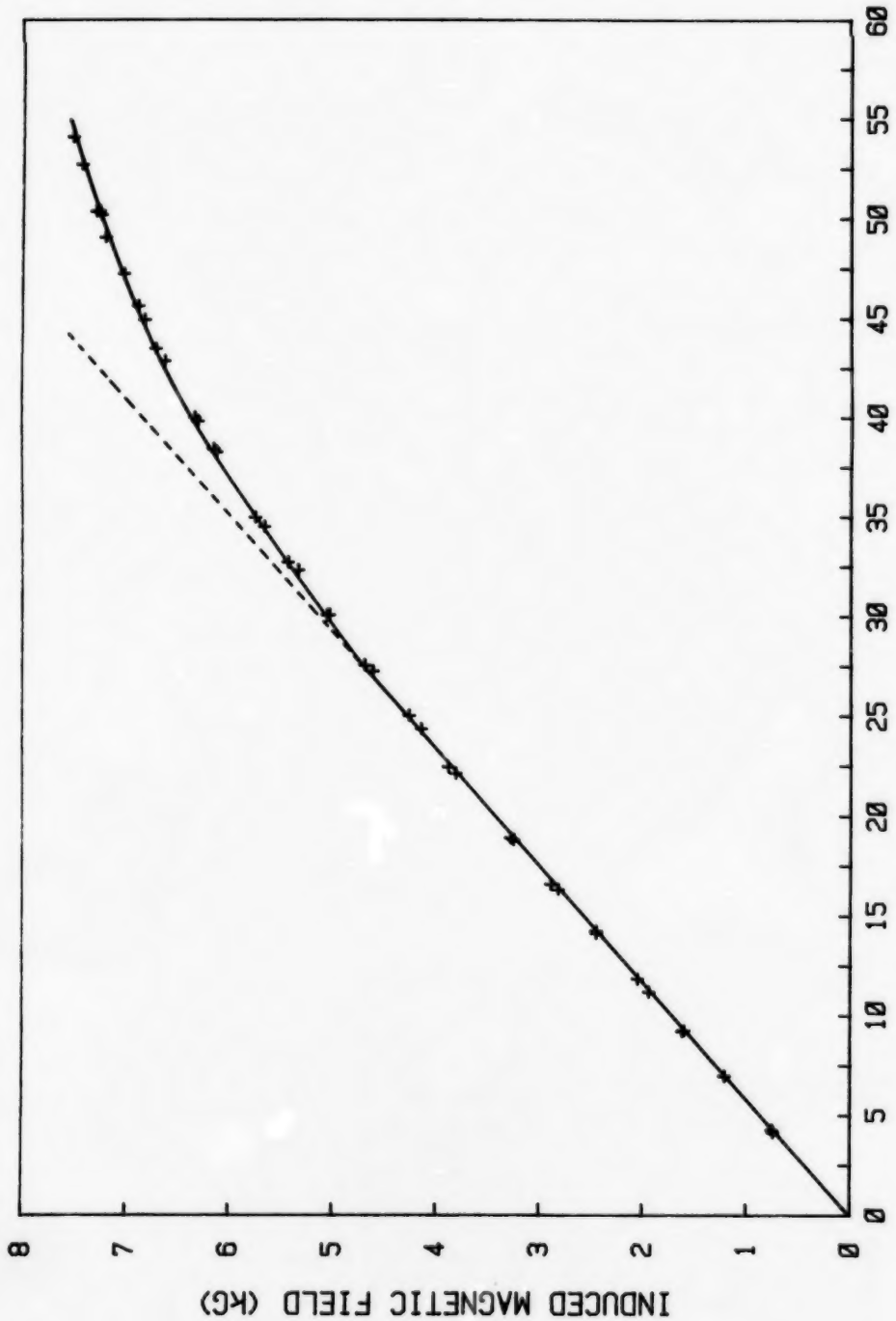


Figure 3: Calibration Curve for the Electromagnet in the Gouy Balance.

If the sample and reference are filled to the same mark in a tube of cross-sectional area A, and are subjected to the same magnetic field, H, under indentical conditions of the Gouy experiment, the following equations (from eqn. [10]) hold, when the tube is surrounded by air:

$$\text{Force (s)} = g.\ \Delta W_s = \tfrac{1}{2}\ A\ H^2\ (K_s - K_{air}) \qquad [13]$$

$$\text{Force (r)} = g.\ \Delta W_r = \tfrac{1}{2}\ A\ H^2\ (K_r - K_{air}) \qquad [14]$$

where $K_{air} = 0.029 \times 10^{-6}$ c.g.s. unit (emu-ml^{-1})

Combining [13] and [14] yields

$$\frac{\Delta W_s}{\Delta W_r} = \frac{K_s - K_{air}}{K_r - K_{air}} = \frac{\chi_s d_s - K_{air}}{\chi_r d_r - K_{air}} \qquad [15]$$

Hence

$$\chi_s = \frac{\chi_r d_r - 0.029 \times 10^{-6}}{\Delta W_r} \cdot \left(\frac{\Delta W_s}{d_s}\right) + \frac{0.029 \times 10^{-6}}{d_s} \qquad [16]$$

or

$$\chi_s = (\text{tube constant})\ \frac{\Delta W_s}{d_s} + \frac{0.029 \times 10^{-6}}{d_s} \qquad [17]$$

This equation is used readily in computing the susceptibility of a liquid sample to a liquid reference, as liquids are "packed" up to a mark in the tube under identical conditions. The evaluation of a constant for a tube and its repeated use in a series of measurements simplify the calculation of the susceptibility.

With solids, it is almost impossible to powder them to the same particle size and to pack them uniformly up to the same mark in the tube; this introduces variations in the volume of paramagnetic air held in the pockets of the sample. Hence, a correction must be made for the susceptibility of air pockets in the powdered solid by introducing the contribution, $K_{air}(1-W_s/V\ .\ d_s)$ due to the air enclosed per mL of the solid-air mixture.

The susceptibility of a powdered solid relative to a liquid reference is thus computed from the following relationship, which is based on a derivation by French and Harrison (31):

$$\chi_s = \frac{\chi_r \cdot d_s - 0.029 \times 10^{-6}}{\Delta W_r} \cdot \frac{\Delta W_s}{W_s} \cdot \frac{W_r}{d_r} + \frac{0.029 \times 10^{-6}}{d_s}$$

$$= (\text{tube constant}) \frac{\Delta W_s}{W_s} \cdot \frac{W_r}{d_r} + \frac{0.029 \times 10^{-6}}{d_s} \qquad [18]$$

For a higher degree of accuracy, another correction must be included to account for the situation that the volume of the solid packed up to a mark will be less than that of the reference liquid by an amount equal to the volume of the meniscus. However, for the precision required in this study, this extra correction is not necessary.

3.4 ERROR ESTIMATION

In the calibration of the magnetic field, the applied voltage could be monitored to ± 0.02 volts in the digital readout, and the magnetic field could be measured to ± 0.03 kG, and yields three significant figures in each reading.

The density of the samples (liquid and solid) are measured by first calibrating the volume with water, and then dividing the weight of sample used by this calibrated volume. Therefore the error in density measurement is governed by how precise the weight was measured (which is less than 0.01%). However, due to the difference in packing (especially for solid samples), this error in density should be estimated as the standard deviation of the packing densities for the same solid. In this case, the standard deviation is estimated to be 2%, or ± 0.02 gm/ml.

The calculated mass magnetic susceptibility (χ) has an estimated error of ±0.02 emu-g^{-1}. However, the true mass magnetic susceptibility χ_{true} (the value extrapolated at infinite field strength in the χ vs 1/H plot) has an estimated error of about ± 0.05 emu-g^{-1} because of the error induced during the least square fit of the data points. It is believed that the second decimal point may not be significant after all of the arithmetic manipulation. Therefore only one decimal place is reported for K, the volume susceptibility. This does not imply that the volume susceptibility values are less precise. Usually in Gouy balance measurements, the error is expected to be about 1-5% (11). This is about the same order of magnitude reflected in the above calculation.

4.0 RESULTS AND DISCUSSION

4.1 CALIBRATION I: MAGNETIC SUSCEPTIBILITIES OF SOLIDS

Since it is impossible to monitor the magnetic field (by a gaussmeter) while the magnetic measurement was being carried out, the applied voltage was measured instead and the field strength was intrapolated from the calibration curve on Figure 3. The change in weight of the samples were measured over a range of magnetic fields (from 1.0 KG to 7.5 KG). In general, the relationship between the change in weight and the magnetic field strength is quadratic in nature, consistent with theory (11). A typical plot for some reference standards is shown in Figure 4.

In this study, benzene ($\chi = -0.702 \times 10^{-6}$ emu-g^{-6}) is used as reference standard for all liquid samples as is recommended (32) while mercury tetrathiocyanatocobaltate, $HgCo(NCS)_4$ ($\chi = 16.44 \times 10^{-6}$ emu-g^{-1}) was used for solid powder samples. The latter was chosen as a standard because of its readily available purity and its stability in moist air (33).

For liquid samples, the tube constant was evaluated first via eqn. [17], i.e.

$$(\text{tube constant})_{xkG} = \frac{\chi_{benzene} \cdot d_{benzene} - 0.029 \times 10^{-6}}{(\text{weight change of sample})_{xkG}} \qquad [19]$$

in which xkG denotes the particular field strength being used. Then the magnetic susceptibility of the samples under investigation could be calculated by eqn. [17].

If the calculated χ was plotted against the reciprocal of the magnetic field H, the intercept on the χ-axis (i.e. at infinite field strength), would yield the true magnetic susceptibility, χ_{true}. The magnetic susceptibility calculated for laboratory deionized distilled water using this method is -0.73×10^{-6} emu-g^{-1}, which deviates only 1.7% from the literature value of -0.72×10^{-6} emu-g^{-1} (11).

For solid samples, the tube constants were calculated using eqn [18], and the true magnetic susceptibilities were evaluated similarly. Table 1 summarizes the true magnetic susceptibility for some chemicals measured. It could be observed that the measured χ_{true} for $CuSo_4 \cdot 5H_2O$ is remarkably close to the literature value of 5.85×10^{-6} emu-g^{-1} (34).

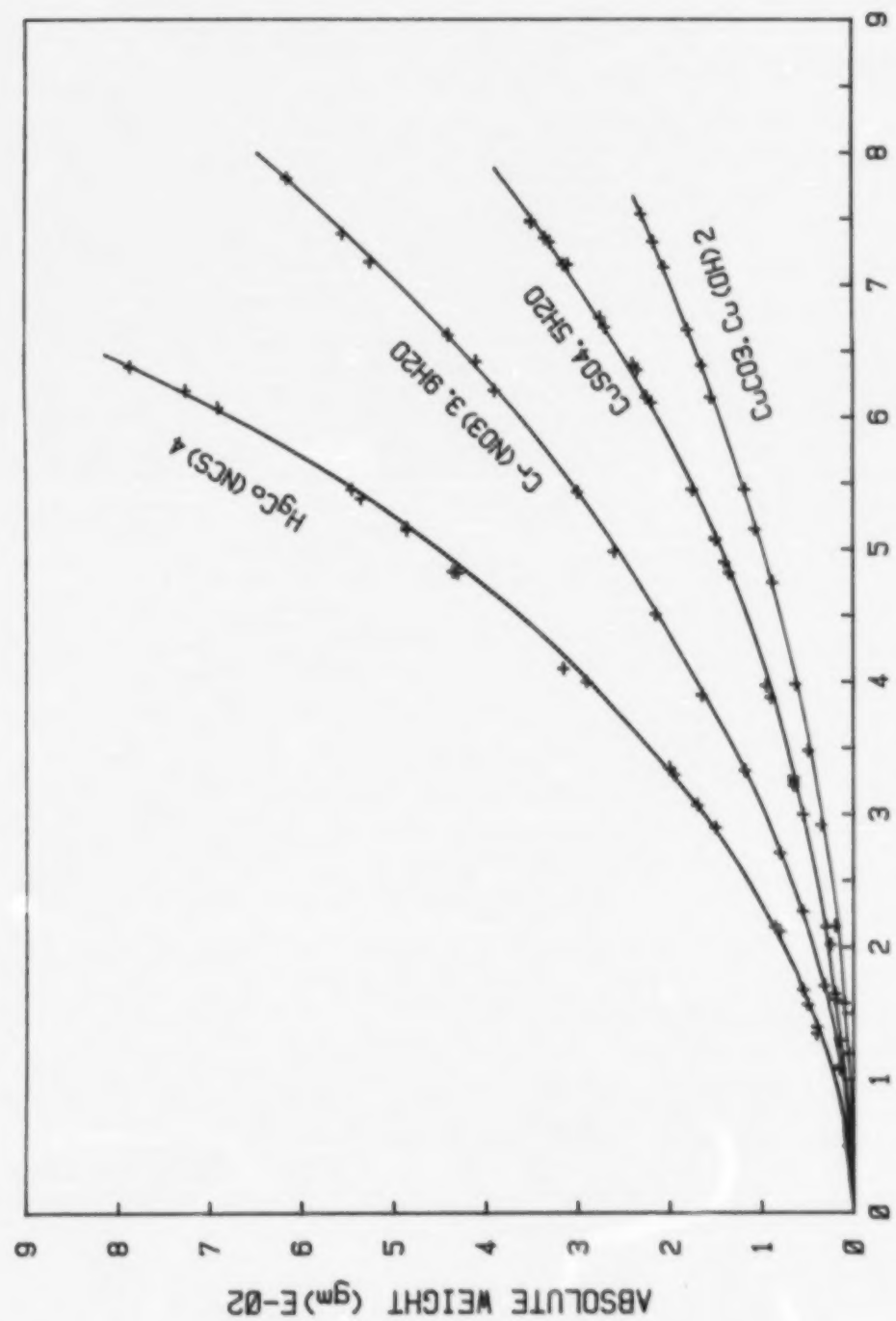


Figure 4: Relationship Between Weight and the Applied Magnetic Field for Paramagnetic Species.

TABLE 1

Magnetic Susceptibilities of Some Chemicals
(in emu-g^{-1})

	$\chi_{true} \times 10^{-6}$	Lit. Value ($\times 10^{-6}$)	Standard
H_2O	-0.733	-0.72	benzene
$Cr(NO_3)_3.9H_2O$	14.8	N.A.	$HgCo(NCS)_4$
$CuSO_4.5H_2O$	5.77	5.85	$HgCo(NCS)_4$
$CuCO_3.Cu(OH)_2$	10.2	N.A.	$HgCo(NCS)_4$

4.2 CALIBRATION II: MAGNETIC SUSCEPTIBILITIES OF SOLUTIONS

In the process of establishing calibration standards for the Gouy balance, a special problem arises for the charcoal samples. All the chemical impregnants are dispersed on the charcoal surface and inside the micropores. In effect, this represents a "chemically" dilute system. However, the distribution of the copper, chromium and silver on the charcoal may be in cluster forms (maximum magnetic interaction) or in a finely divided state (minimum magnetic interaction). Although it would be difficult to evaluate for the cluster forms, the finely divided state may be approximated as in a solution state; this analogy may not be entirely appropriate but it will have to suffice for our purposes. Solid solutions (e.g. glass, ceramics) containing finely-divided chromium salts are difficult to prepare and even more difficult to analyse (35). It should also be pointed out that a solid mixture of charcoal and chromium salt would not yield a good calibration standard. The reasons being, first it is difficult to obtain a homogeneous mixture of both, and this will affect the response of the mixture in a magnetic field. Secondly, a solid mixture of both does not necessarily reproduce the situation as in the impregnated charcoal.

Two solutions of inorganic salts, namely chromium nitrate, $Cr(No_3)_3.9H_2O$ and copper sulfate, $CuSO_4 \cdot 5H_2O$ were investigated in this report. Stock solutions, made up by weighing out quantities of the above salts, were diluted to the other concentrations. The calculated magnetic susceptibilities, χ_{true} are plotted as a function of the concentration of the salts as in Figures 5 and 6 using data in Table 2 and 3. The densities of the prepared solutions were measured by means of a pycnometer. Due to the poor solubility of $CuSO_4 \cdot 5H_2O$ in water, only a limited concentration range was viable.

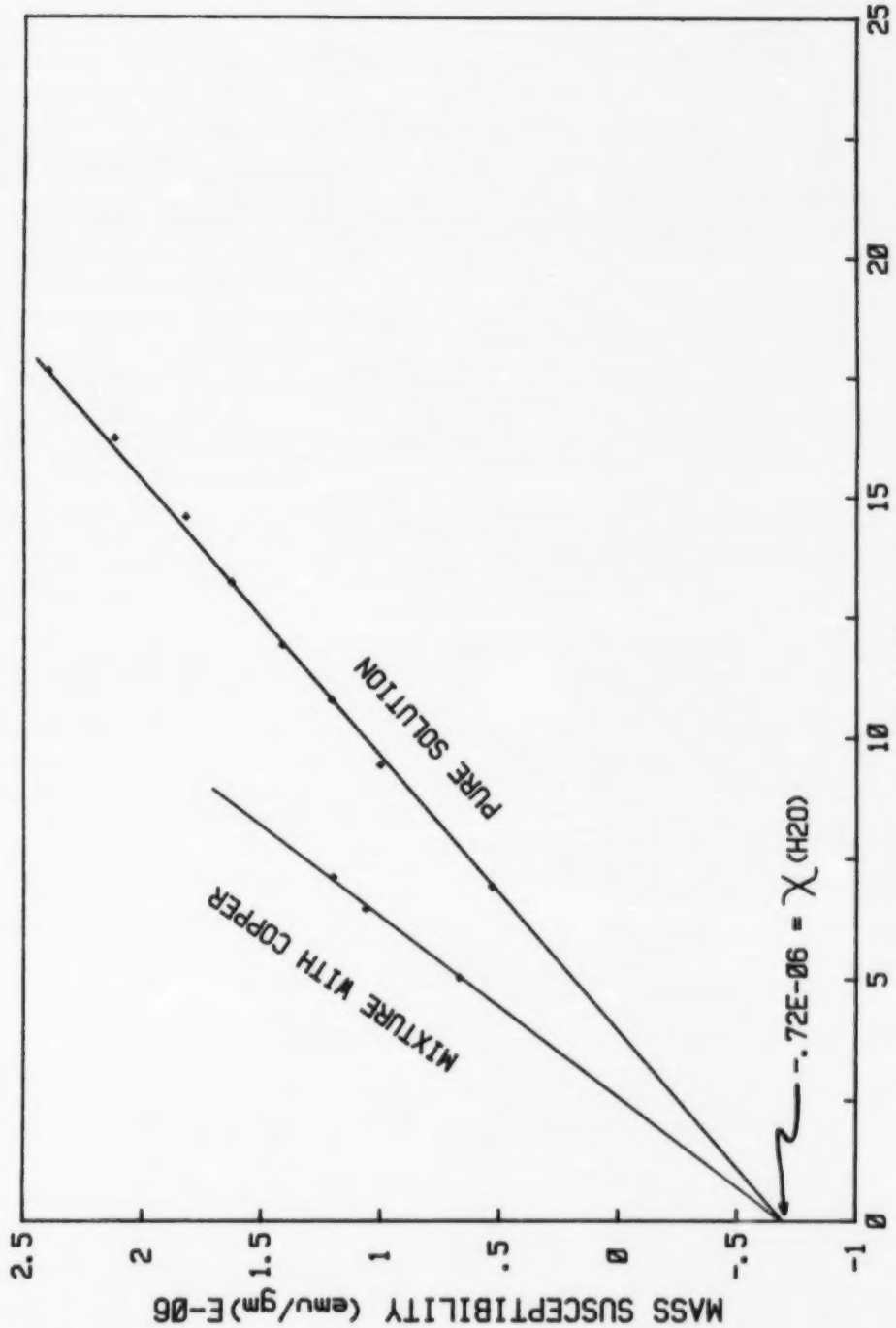


Figure 5: Mass Magnetic Susceptibilities vs % Cr(NO)$_3$ in Solutions.

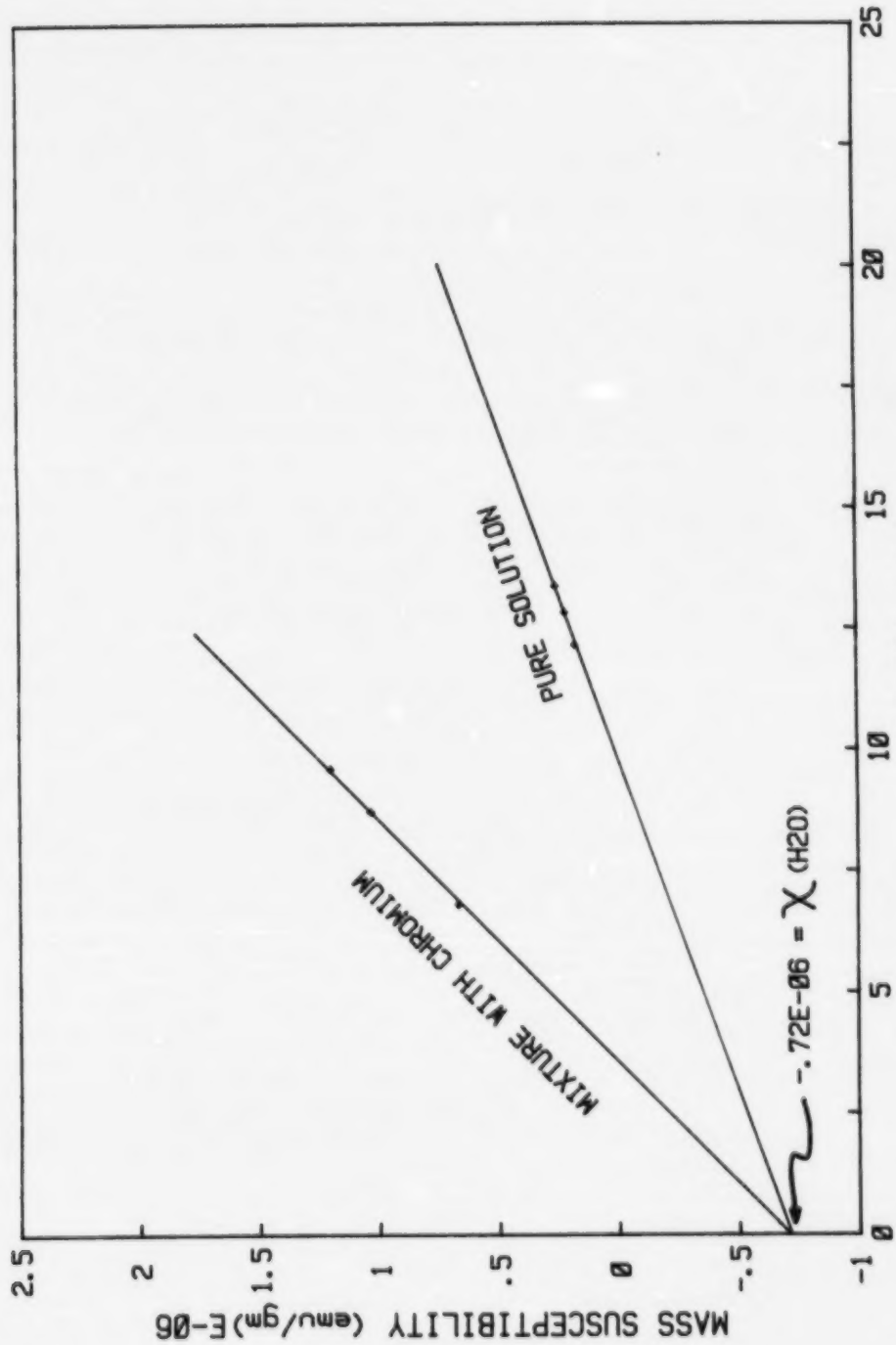


Figure 6: Mass Magnetic Susceptibilities vs % $CuSO_4$ in Solutions.

TABLE 2

Magnetic Susceptibilities of Chromium Nitrate Solutions

Concentration in weight % of $Cr(NO_3)_3$	Density gm/ml	Susceptibility χ_{true}, emu-g^{-1} x 10^{-6}	Molar Susceptibility χ_M, emu-$mole^{-1}$ x 10^{-3}
17.64	1.15	2.39	6.77
16.22	1.13	2.12	6.71
14.57	1.12	1.82	6.68
13.21	1.10	1.62	6.81
11.92	1.10	1.41	6.87
10.78	1.08	1.20	6.85
9.43	1.07	1.00	7.01
6.91	1.05	0.53	6.96
			Avg = 6.83×10^{-3} emu-$mole^{-1}$

TABLE 3

Magnetic Susceptibilities of Copper Sulfate Solutions

Concentration in weight % of $CuSO_4$	Density gm/ml	Susceptibility χ_{true}, emu-g^{-1} x 10^{-6}	Molar Susceptibility χ_M, emu-$mole^{-1}$ x 10^{-3}
13.37	1.14	0.26	1.64
12.83	1.13	0.22	1.64
12.15	1.12	0.17	1.66
			Avg = 1.65×10^{-3} emu-$mole^{-1}$

The magnetic susceptibility of a solution is known to be an additive function of the susceptibilities of each component in the solution (13). After corrections have been made for the contribution of water, the calculated molar susceptibilities are given in the last column in Tables 2 and 3. The measured value of the molar susceptibility for $CuSO_4.5H_2O$ is significantly higher than the reported value of 1.46×10^{-3} emu-mole^{-1} (34). There is no reported value of χ_M for $Cr(NO_3)_3.9H_2O$, however, the magnetic susceptibility calculated from this χ_M value is 15% higher than the value reported in Table 1. The difference may primarily be due to the fact that no attempt was made to accurately analyze the samples of the hydrate used. Also, it is not unusual that the substances subjected to magneto-chemical investigation may contain traces of ferromagnetic impurities. Because chemical or spectroscopic purity is no guarantee of "magnetic purity", erroneous data may result.

It should be pointed out that the susceptibility of a mixture is not always a linear function of concentration (11). For some special cases, e.g. the $NiCl_2$ solution, the susceptibility of this solution is found to be independent of concentration near 30% $NiCl_2$ by weight (36). Hence, such a solution may be used conveniently for calibration purposes. In the present case, the chromium nitrate and copper sulfate solutions do not seem to behave like the nickel chloride solution, therefore the additivity law does not apply here.

From the values of the molar susceptibilities, the magnetic moment μ, of the substance could be evaluated by:

$$\text{Magnetic moment (Bohr magnetons)} = 2.83 \sqrt{\chi_M \cdot T} \qquad [20]$$

where T is the temperature of measurement in °K. For $CuSO_4.5H_2O$, the magnetic moment is found to be 1.97 Bohr magnetons as compared to a value of 1.73 calculated for of one unpaired electron in the Cu (II) ion. Similarly, μ of $Cr(NO_3)_3$ is calculated to be 4.04, as compared to the value of 3.87 calculated for three unpaired electrons for the Cr (III) ion. These results are consistent with predictions from theoretical treatments (11,13).

Therefore, since it was not conclusive whether the additivity law applies, a final experiment was carried out. Magnetic susceptibilities were measured for solutions containing both the $CuSO_4.5H_2O$ and $Cr(NO_3)_3.9H_2O$ salts. The solutions were prepared by serial dilutions of a master solution. The results are summarized in Table 4. Super-imposing these data on the graphs on Figures 5 and 6 indicate that the measured magnetic susceptibility is not the sum of the individual susceptibilities due to $CuSO_4$ or $Cr(NO_3)_3$.

TABLE 4

Magnetic Susceptibilities of a Mixture of Solutions Containing $Cr(NO_3)_3.9H_2O$ and $CuSo_4.5H_2O$

Weight % $CuSO_4$	Weight % $Cr(NO_3)_3$	Density (gm/ml)	Magnetic Susceptibilities $\chi_{true} \times 10^{-6}$ emu-g^{-1}
9.06	7.10	1.21	1.20
8.72	6.45	1.09	1.09
6.81	5.03	0.65	0.67

This result is not surprising as it was pointed out earlier, that the linearity between magnetic susceptibility and the concentration of the solutions is not always observed. The validity of Wiedeman's Law (11) in which the mass susceptibility χ, of a mixture of components with susceptibilities χ_1, χ_2 ... χ_n and weight fractions P_1, P_2, ... P_n may be expressed as

$$\chi = \chi_1 P_1 + \chi_2 P_2 + \ldots + \chi_n P_n \qquad [21]$$

is obeyed closely by mechanical mixtures and solutions of diamagnetic substances. However this stipulates little or no interaction takes place either between molecules or ions of the components or between these and the solvent. This stipulation makes it imperative that caution be exercised in deducing the susceptibility of a solute from that of the solution. The application of the law to solids or liquid solutions containing paramagnetic ions becomes even more difficult as the interactions amongst ions or between ions and the solvent become quite pronounced. In such cases, it is therefore necessary to ascertain that the system is "magnetically dilute". Although the ions of the first row transitional elements have been extensively studied and their single ion non-interacting magnetic properties very well documented, one must also determine the behaviour of magnetically coupled systems (e.g. magnetic exchange of bi-nuclear complexes).

4.3 MAGNETIC SUSCEPTIBILITIES OF CHARCOAL SAMPLES

Two kinds of ASC-whetlerites (with or without the co-impregnation of triethylenediamine, TEDA) were studied. These charcoals were either commercially supplied by Calgon Carbon Corporation or custom-made in this laboratory. The Calgon charcoals are denoted by CAL- followed by a batch number in the following text except BPL-charcoal, which is a base charcoal with no impregnation history. The custom made ASC-whetlerites were prepared by impregnating the BPL charcoal with solutions containing the desired impregnants such as copper, chromium (trivalent or hexavalent) and silver at allowable concentrations. The detail of this impregnation procedure and its accompanied hardware will be discussed in another forthcoming report. The custom-made charcoals are denoted by DREO-, followed by a batch number.

All ASC charcoals are loaded with various levels of copper, chromium, and silver. The copper is believed to be in the form of CuO or Cu_2O (6,7). The chromium is impregnated in the form of chromic anhydride, CrO_3 although some of it will be subsequently converted to Cr_2O_3 due to the reducing power of charcoal, aging, or other unknown factors during the impregnating procedure. Silver is probably adsorbed onto the charcoal as silver ion. However, due to its small magnetic susceptibility (34) and its small concentration on charcoal (~ 0.05% by weight), silver is ignored in this study.

Chromium in its highest oxidation state, Cr (VI) has a very small magnetic susceptibility (34), e.g. CrO_3 has $\chi_M = 40 \times 10^{-6}$ emu-mole^{-1}, and some chromate salts are actually diamagnetic e.g. $CdCrO_4$. On the other hand, Cr (III) has very high magnetic susceptibility because of its three unpaired electrons. Even a non-ionic compound like Cr_2O_3 has $\chi_M \simeq 2000 \times 10^{-6}$ emu-mole^{-1}. Copper compounds usually have lower magnetic susceptibilities. Cu_2O is diamagnetic while CuO only has an χ_M value of 240×10^{-6} emu-mole^{-1}. Since charcoal is diamagnetic (carbon in the forms of graphite, diamond or amorphous are all diamagnetic (34)) and if both copper and chromium impregnate on charcoal as oxides, then the single major contributor to the measured magnetic susceptibility of ASC-whetlerite is due to Cr_2O_3 alone.

The concentration of the copper and the trivalent chromium, Cr (III) given in Tables 5 and 7 were analyzed by standard procedures (37). These analyses were performed on dry, sealed charcoals within 15 days of the magnetic susceptibility measurements, therefore the effect of aging could be neglected. As the charcoal ages, one would expect the concentration of Cr (III) to increase (from the reduction of Cr (VI)) and thus the bulk magnetic susceptibility of the charcoal to increase also. In the same tables, the density given was the packing density of the charcoal inside

the 5 mm o.d. nmr tube as opposed to the apparent density measured by the ASTM method (38). The density was measured by subtracting the weight of an empty nmr tube from the weight of the tube after it was filled with charcoal to the mark, and then dividing by the volume of the tube (calibrated with water at 24°C). By observing the packing density of the same charcoal sample under investigation several times, the "reproducibility" of the packing procedure could be monitored. The packing densities generally had a standard deviation of less than 2%, indicating that the packing procedures were very consistent.

The purpose of this feasibility study is then an attempt to correlate the concentration of copper and chromium (as Cr (III)) with the bulk magnetic susceptibility measured for the impregnated charcoal.

4.3.1 ASC-Whetlerites

Table 5 summarizes the results from the magnetic susceptibility measurements on the ASC-whetlerites. The following observations were noted:

1) All the commercially prepared charcoals have packing densities around 0.68 gm/ml. Wet charcoal seems to pack the same or slightly lower than the corresponding dry charcoal. This is probably due to the charcoal agglomerating, and therefore the packing density depends on how wet the charcoal is.

2) The mass magnetic susceptibilities of the charcoal samples are shown in column 5 in Table 5. These data show variations and some anomalies e.g. the charcoal CAL-1048 actually has a lower mass susceptibility than the base charcoal. It would be common sense to expect that with the impregnation of paramagnetic species like copper and chromium, the mass susceptibility would increase for the charcoal samples (from the base charcoal). However, this discrepancy could be very easily explained by the differences in the packing densities among the different charcoal samples. Since all the samples under measurement were packed to pretty well the same volume, but varied widely in weight, it appears that K, the volume susceptibility (emu-ml^{-1}) may be a better choice as a base unit. The volume susceptibilities ($K = \chi \cdot$ density) of the different charcoals are listed in the last column in Table 5.

3) It is apparent that the K for base charcoal is not close to zero, indicating some residual paramagnetism. Carbon in either the diamond, graphite, or amorphous form is diamagnetic (34). This may indicate the presence of ash or iron impurities. A neutron activation analysis of the charcoals are presented in Appendix B. Also, after exposure to moisture, the charcoal samples show higher volume susceptibilities. This is peculiar since water is diamagnetic and from the additivity

TABLE 5

Magnetic Susceptibilities of ASC-whetlerites

Charcoal	% Cu	% Cr(III)	Packing Density (gm/ml)	Magnetic Susceptibilities	
				Mass, χ_{true} ($emu\text{-}g^{-1}$)	Volume, K ($emu\text{-}ml^{-1}$)
BPL	0	0	0.51	22.3	11.3
BPL (wet)	0	0	0.48	25.6	12.2
CAL-1048	7.23	1.26	0.68	21.0	14.4
CAL-1048 (wet)	7.23	1.26	0.68	23.8	16.2
CAL-1034	7.58	1.30	0.68	28.2	19.0
CAL-1275	8.50	1.30	0.68	27.5	18.6
DREO-01	6.32	0.77	0.60	21.2	12.8
DREO-02	8.07	2.85	0.65	22.6	14.7
DREO-03	7.50	0.26	0.64	20.6	13.2
DREO-04	9.25	0	0.59	21.9	13.0
DREO-05	0	3.85	0.59	24.2	14.2
DREO-06	0	1.85	0.54	22.4	12.1
DREO-07	0	1.94	0.54	23.7	12.7
DREO-08*	0	3.40	0.57	23.4	13.4
DREO-09*	0	3.50	0.57	23.4	13.2

Note: * Indicates that impregnating solution contains Cr(III) only. The other solutions all contain Cr(VI).

All copper and chromium analysis were performed within 15 days of the magnetic susceptibility measurements.

law of magnetic susceptibilities, one would expect that the measured susceptibility might be lowered rather than increased. One simple explanation would be that the adsorbed (or absorbed) water leaches out the impregnants on the charcoal and re-distributes them in such a way that the bulk magnetic susceptibility is enhanced. It was found that Cu_2O is diamagnetic (χ_M = -20.6 emu-mole^{-1}) and CuO is slightly paramagnetic (χ_M~ 240 emu-mole^{-1}), but the χ_M is one magnitude bigger for the sulfate or chloride salt (34). A solvation process in which Cu^+ or Cu^{2+} are formed will increase the magnetic susceptibility. This reasoning is also substantiated by the observation for some chromium and iron salts, that the susceptibility in the colloidal state is somewhat higher than that in the powder form (39).

4) Looking at the commercially-supplied charcoals alone, it seemed that at constant chromium concentration, variations in copper concentration do not yield significant change in volume susceptibility, as shown for CAL-1034 and CAL-1275. However, at the same copper concentration, variation in chromium concentration yields almost a 5 emu-ml^{-1} change in volume susceptibility, as shown in Table 5 between CAL-1048 and CAL-1275, and between CAL-1048 and CAL-1034.

It should be stressed that some reservation must be made in making the above interpretation. Without the detailed knowledge of the history of the charcoal samples (e.g. the commercial charcoal samples in the present case), some of this analysis may be futile. As the charcoal ages, one would expect that the ionic concentrations (of Cu^+, Cu^{2+}, Cr^{3+}) may increase and thus alter the magnetic susceptibility. The degree to which the susceptibility changes depends on factors such as stereochemistry (of the impregnants), and magnetic interactions. The additivity law may not even apply in some cases, as was shown in section 4.2.

For the custom-made impregnated charcoals, the data in Table 5 show more variations:

1) In general, the packing densities and the volume susceptibilities for these charcoals are lower than the commercially-prepared charcoals even though the concentrations of copper and chromium are compatible. This may be attributed to the differences in preparation procedure, use of chemicals, etc.

2) For the custom-made charcoals impregnated with chromium only (Cr (III) or Cr (VI)) as in DREO-05 to DREO-09, the volume susceptibilities vary very little (between 12 and 14 emu-ml^{-1}) although the concentration of Cr (III) almost doubles (between DREO-05 and DREO-07).

3) DREO-04 which contains only copper as the sole impregnant, has a volume susceptibility of 13.0 emu-ml^{-1}. It would appear that at such a high concentration of copper (normal loading level for copper is about 8%), the volume susceptibility of this charcoal behaves like that of a charcoal impregnated with chromium alone.

4) For custom-made charcoals impregnated with both copper and chromium, there is no significant increase in the volume susceptibility compared to the charcoals containing either impregnants only. The volume susceptibility values of 18-19 emu-ml^{-1} obtained for the commercial charcoals (as in CAL-1034 and -1275) are not observed here. Once again, this may be attributed to differences in preparation, aging and other effects.

4.3.1.1 Statistical Analysis for the Custom-Made Charcoals

The qualitative assessment given above certainly indicates some general trends relating the loading levels of the chemical impregnants on charcoal with respect to the measured volume magnetic susceptibility. Quantitatively, a multiple linear regression analysis was performed to correlate the magnetic susceptibility data with the concentrations of copper and chromium. The detailed statistics are shown in Table 6. The proposed model is:

$$\text{Volume susceptibility} = 11.24 + 0.64\,[\text{Cr(III)}] + 0.20\,[\text{Cu}] \qquad [22]$$

where the square brackets denote concentrations in weight %. The t-test indicates that all the partial regression coefficients are significantly different from zero, and the values of 11.24, 0.64 and 0.20 are obtained not due to chance. The regression model is significant (from the analysis of variance of the regression) in that 91% (from the multiple correlation coefficient, R^2) of the residuals are explained by this regression model.

One of the major limitations in this regression model is that all the variables belong to a type 2 population i.e. they are not normally distributed and may even be bivariate. Thus all the statistics involving the sample variance may be low and require adjustments.

This linear model further substantiates that the concentration of chromium is a major contributor to the bulk magnetic susceptibility of the impregnated charcoal. The coefficient for [Cr (III)] is three times that of the [Cu] from eqn. [22]. This means that each concentration unit increase for Cr (III) contributes an effect (to the magnetic susceptibility of the bulk charcoal) that is equivalent to an increase of three concentration units of copper. This observation may be attributed to the fact that the chromium species in the impregnated charcoal has three unpaired electrons, while only one unpaired electron exists for the copper species.

TABLE 6

Statistical Analysis with the Custom-made ASC-Whetlerites
The Linear Regression Model:
Volume Susceptibility = 11.24 + 0.64 [Cr(III)] + 0.20 [Cu]

Test Statistics	Interpretation
Coefficient of Multiple Determination $R^2 = 0.91$	Indicates 91% of the error is explained by this model.
Analysis of Variance of the Regression $F_0 = 35.12$	At 99% confidence interval $F_{0.01,2,7} = 9.55 << F_0$ ∴ Both variables contribute to the model
Two sided t-test on all coefficients: the constant term $t_{01} = 46.65$ the coefficient for [Cr(III)] $t_{02} = 7.83$ the coefficient for [Cu] $t_{02} = 6.50$	At 99.999% confidence interval $t_{0.0005,7} = 5.405 <$ all t_0's ∴ All coefficients are significantly differed from zero, i.e. all contribute to the model.
Durbin-Watson Statistics = 2.84	At 99% confidence interval $d_L = 1.54 << 2.84$ ∴ There is no serial correlation on the stochastic error term. i.e. an independent random variable.

A curvilinear relationship could also be estimated with the data from Table 5 as follows:

$$\text{Volume susceptibility} = 11.31 + 0.49\,[\text{Cr (III)}] + 0.21\,[\text{Cu}] + 0.04\,[\text{Cr (III)}]^2 - 0.01\,[\text{Cu}]^2 + 0.06\,[\text{Cr (III)}]\,[\text{Cu}] \qquad [23]$$

with a R^2 (i.e. the multiple correlation coefficient) of 0.91. However, the interpretation of this model is more complicated, due to the addition of three more variables. Moreover, the same value of R^2 is obtained without a decrease in the residual variance. This probably indicates that the use of this model is not justified.

When all of the data in Table 5 were regressed together (i.e. both commercially-supplied and custom-made charcoals), the 'goodness of fit' by a least square linear regression model drops drastically to a R^2 of 0.44. Although the value of 0.44 for R^2 is significant at 1% significance level, the proper interpretation would be that this may not be the best model representing the data.

This lack of fit was actually explained in section 4.3.1, i.e.

1) The packing densities of both the commercially-supplied charcoals and the custom-made charcoals are quite different;

2) The values of volume susceptibility obtained are quite different for the two types of charcoal.

This implies that these two types of charcoal should be evaluated separately.

4.3.2 ASC-Whetlerites Co-impregnated with TEDA

Table 7 summarizes the magnetic susceptibility measurement data of the ASC-whetlerites which are also impregnated with TEDA. TEDA, or more properly 1,4-diazabicyclo [2,2,2] octane, has received the attention of British, American and Canadian investigators as a supplementary additive for CK-protection in gas-mask usage. It is in terms of general interest that the magnetic susceptibility studies were extended to the TEDA-loaded ASC-whetlerites, as the interpretation of the resulting data would be extremely complicated. The reasoning for this will be elaborated on later. Once again, the charcoals investigated were either from commercial source (Calgon Carbon Corporation) or custom-made from this laboratory.

TABLE 7

Magnetic Susceptibilities of ASC Whetlerites
Co-impregnated with TEDA

Charcoal	% Cu	% Cr(III)	TEDA Content Wt%[b]	Packing Densities (gm/ml)	Magnetic Susceptibilities	
					mass, χ_{true} emu-gm^{-1}	Volume, K emu-ml^{-1}
CAL-1.5[a]	8.38	1.09	1.2	0.69	28.2	19.4
CAL-3[a]	8.31	1.22	2.7	0.68	22.5	15.3
CAL-6[a]	7.90	1.26	5.4	0.72	17.7	12.7
CAL-10[a]	7.72	1.23	9.2	0.72	22.1	16.0
DREO-10	0	2.75	6.2	0.66	24.2	16.0
DREO-11	0	0	6.2	0.58	18.2	10.5
DREO-12	0	3.60	8.0	0.64	20.7	13.5

Note: a) Commercially-supplied ASC whetlerites co-impregnated with TEDA; the number after CAL indicates the loading level of TEDA (as suggested by the manufacturer).

b) The true TEDA content determined in this laboratory, using DND specification (37).

For the commercially-supplied charcoals, the volume susceptibility data show variations. For example, CAL-6 and CAL-10 both have approximately the same concentrations of copper and chromium, an increase in TEDA loading (from 6 to 10%) is reflected with an increase of 3.3 emu-ml^{-1} in susceptibility. However, the sample CAL-1.5 has the highest volume susceptibility (19.4 emu-ml^{-1}) although it has the lowest TEDA content and about the same concentrations of copper and chromium as CAL-3 and CAL-6.

Combining these data from commercial charcoals with those of the custom-made charcoals, a general picture can be drawn about these ASC-charcoals co-impregnated with TEDA:

1) The volume susceptibility of DREO-11 (BPL charcoal with 6% TEDA) is the lowest so far (10.5 emu-ml^{-1}) compared to the value of 11.3 emu-ml^{-1} for BPL-charcoal (from Table 5). This indicates that TEDA, being diamagnetic (as with all organic molecules) (36) lowered the magnetic susceptibility of the bulk charcoal. This is substantiated by the observations in DREO-10 and DREO-12 in which chromium and TEDA are the sole impregnants in both samples. DREO-12 which has higher chromium and TEDA content actually has a lower volume susceptibility.

2) For the commercial charcoals, the observation indicates a trend in the opposite direction. This must be attributed to the differences in preparation of the charcoals.

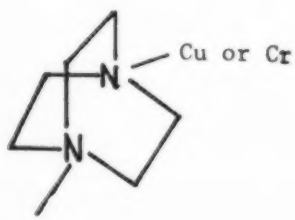
This brings out an important difference between the ASC-Whetlerites and ASC-Whetlerites with TEDA. It is believed that TEDA by itself is strongly adsorbed on the charcoal surface (40). However in the presence of Cu (I), Cu (II) and Cr (III), organometallic complexes may have been formed. Since the lone pair of electrons of both the nitrogen atoms on TEDA faces away from each other, it is possible for TEDA to form a unidentate ligand with copper or chromium (as in B or C) or remain as the free form (as in A).

Cu or Cr
on
Charcoal

A

Cu or Cr
on
Charcoal

B



Cu or Cr
on
Charcoal

C

Depending on the configuration and stereochemistry of these complexes, magnetic susceptibilities of these complexes vary (14,16,20), and depending on the distribution of these complexes, they may actually interact magnetically and yield some very complicated results.

It is well known that the stereochemistry of an organometallic complex affects the magnetic moment of the complex. For example, the octahedral complex of Co^{2+} (in $Co(H_2O)_6^{2+}$ ion) is pink and has a magnetic moment of 4.8-5.2 Bohr magnetons, while the blue tetrahedral complex of $[CoCl_4]^{2-}$ has a smaller magnetic moment of 4.3-4.7 Bohr magnetons only. This arises from the fact that the number of unpaired electrons are different because the five 3d orbitals have different degeneracy (because of different symmetries) from the ligand field theory consideration. Noting the direct relationship between χ and the magnetic moment (eqn. [20]), it is obvious that there is a strong dependence of χ on the stereochemistry of the complex.

On the charcoal surface, one would not expect the formation of any high-symmetry complexes (e.g. octahedral or tetrahedral) between the copper and chromium ions with TEDA. Complexes of intermediate symmetry (tetragonal or square planar), lower (e.g. C_2) symmetry, and no symmetry would have magnetic moment (and consequently χ) varying over a wide range of values. Therefore, a very complicated scenario results from the co-impregnation of TEDA on the ASC-Whetlerites. The charcoal surface would have a variety of adsorbed species, e.g. TEDA species (diamagnetic), and a variety of copper-TEDA and chromium-TEDA complex of various symmetries.

The research and development of the co-impregnation of TEDA on ASC-whetlerites is only at a preliminary stage in this laboratory. It is anticipated that with more additional data, a similar linear regression model may be established for this special blend of charcoal (as in Section 4.3.1.1).

5.0 CONCLUSIONS

This report has established that the use of a Gouy balance in determining the magnetic susceptibilities of charcoal is feasible. It also shows that the custom-made charcoals prepared by this laboratory are different from the commercially supplied charcoals, although the concentrations of the impregnants are similar. A linear regression model is proposed to correlate the measured susceptibilities of the charcoal with the concentrations of copper and chromium for the custom-made charcoals. The same model also substantiates the hypothesis that the concentration of chromium will contribute significantly more to the bulk magnetic susceptibility than copper. However, for the purpose of non destructive analysis of impregnants on ASC charcoals, magnetic susceptibility would be

best used as a qualitative tool for the assessment of the metal impregnants on charcoal.

Some preliminary results on the magnetic susceptibilities of ASC-whetlerites co-impregnated with TEDA are also presented here. The variation of magnetic susceptibility with respect to varying concentrations of copper, chromium, and TEDA is much too complicated to mathematically model. Preliminary findings confirm that a linear regression model would show the appropriate correlations; this finding requires more data for refinement. The difficulty in interpreting these data is compounded by the fact that it involves a detailed understanding of the organometallic chemistry and ligand field theory that is involved in this complex system.

6.0 RECOMMENDATIONS

6.1 It is recommended that the application of magnetic susceptibility measurement as a non-destructive residual life indicator for aged and/or organic contaminated charcoal filters be further investigated. Based on results obtained in this study there is preliminary evidence that a magnetic susceptometer could be used as a simple pass or fail qualitative indicator of a charcoal bed's residual life. This recommendation requires that statistically significant quantities of data be collected on new, aged, and organically contaminated ASC whetlerite charcoals.

6.2 It is recommended that magnetic susceptibility not be considered a viable analytical technique for the quantitative determination of chromium, copper, or triethylenediamine on whetlerite charcoal.

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APPENDIX A

MAGNETIC SUSCEPTIBILITY MEASUREMENTS WITH COMMERCIAL INSTRUMENTS

All the magentic susceptibility measurements given in this report are specific to the Gouy balance custom-built in this laboratory. Variations in the equipment may introduce discrepancies in the resulting data. One of the ways to avoid this is to employ instruments from a commercial source so that uniformity may be maintained. The other advantages of using commercial instruments include:

(i) the sample-handling involved is usually simpler;

(ii) there are usually very few restrictions about the sample under investigation, e.g. sample sizes, constituents etc;

(iii) all calculations and data manipulations are minimized or computerized e.g. the air surrounding the sample is usually accounted for; and

(iv) a summation of all of the above -- less time consuming.

Two commercial magnetic susceptometers were used on site at the Geological Division of CANMET, whose help is greatly appreciated. One of the susceptometers was a VGF KL-1 magnetic susceptibility bridge. The magnet component is a simple coil in which the samples were inserted. The induced field was measured by balancing this additional field to zero with the aid of a 20-turns potentiometer. The magnetic susceptibility was then read off from the potentiometer (as the ratio M/H). The standard deviation with this instrument was estimated to be about 2 to 5%. Field drift was observed between magnetic susceptibility measurements. This was probably due to the choice of high sensitivity and a small range.

The other instrument used was similar to the above, and manufactured by Sapphire Instruments (Model No. 585GSC-LS). A copper coil 2 ½ cm long and 2 ½ cm in diameter in which the samples were inserted was connected to a black box which in turn was connected to a Compac Plus computer. The black box is a simple monitoring device which measures the field inside the coil. By monitoring the coil with no sample (with only air) and then with the sample inside, the computer calculated the difference in the field strength, and thus χ was computed. The computer also has software to correct for the volume differences among samples. This is done by entering the volume (of the sample) before the measurements are taken. All the susceptibility data from this instrument were measured at least three times so that standard deviations could be evaluated. This

standard deviation is estimated to be about 1% for consecutively repeated measurements. However it was noticed that the reproducibility of the experimental measurements was not very good, and variations of up to 30% were observed in some cases where measurements were made at random. One of the plausible reasons is that the instrument resetting mechanism is not fast enough to accommodate rapid sample changing and slight variations in the volume of sample under investigation.

All charcoal samples were stored in a glass vial 6.5 cm long by 1.9 cm diameter with a plastic screw-on cap. The charcoals investigated were in two forms:

(i) the powder form i.e. the same size used in the Gouy balance experiments; and

(ii) a 12 x 30 mesh size -- the same size that the Calgon charcoals were shipped in (i.e. the size of the charcoal before grinding).

The powder form charcoals were filled to various volume sizes inside the vials, but the pellet form charcoals were filled to the same volumes. The vials containing the charcoal samples were inserted directly into the coil and the measurements were taken. For the two types of charcoals (ASC whetlerites with/without TEDA), the volume susceptibility data were summarized in Table A-1. A correction factor was incorporated into the volume susceptibility values for the powder form charcoals in the VGF KL-1 measurements, because of the volume variations. The four Calgon charcoals which contain TEDA were not measured in the pellet form because no samples were available. For the magnetic susceptibility values using the VGF-KL 1 bridge, the following observations were made:

(1) With the powder form charcoals, the measured volume susceptibility values were in the same order of magnitude with the values obtained from the Gouy balance. However, there were more variations among the data. Similar trends (as shown in Table 5 and discussed in section 4.3) were also observed e.g. CAL-1034 had the overall highest volume susceptibility while BPL (the base charcoal) had the lowest. Some custom-made charcoals e.g. DREO-08 had similar susceptibility values as the commercial charcoals which is not observed in Table 5.

(2) For the pellet forms, similar trends and variations among the data were also observed, although in general, these data appeared to be greater in value than the corresponding ones in the powder form.

(3) For the ASC whetlerites containing TEDA, the anomalies among the data are more pronounced, although these data have the same order of magnitude as those in Table 7. Although DREO-11, which is basically BPL-charcoal with TEDA (no metal impregnants), would be expected to yield the lowest susceptibility value, this was not the case.

These anomalies could be attributed to the differences in packing of the charcoal samples inside the vial (compared to the vigorous packing procedure necessary for the Gouy balance experiments), and the amount of air trapped inside the sample. The glass vial apparently has no effect on the measured bulk susceptibilities. One would expect the pellet form charcoals to show smaller volume susceptibilities due to inefficient packing, i.e. the volumes which should have been charcoal are now occupied by air which has a much smaller volume susceptibility. However, this conjecture is not substantiated from the present observations. Therefore it is apparent that this instrument is not suitable for qualitative and/or quantitative assessment of the charcoal samples.

For the Sapphire Instrument susceptometer, the following observations were noted:

(1) All the magnetic susceptibility data for the powder form charcoals are 10 to 20 times bigger than the corresponding ones measured by the VGF KL-1 susceptibility bridge. The BPL charcoal does not have the lowest susceptibility value which probably indicates that the other data may be erroneous.

(2) Although some of the custom-made charcoals in the powder form show lower susceptibilities than the commercial charcoals, these data show too much variation to be of any qualitative use.

(3) The magnetic susceptibility measurements for the pellet form charcoals from this Sapphire Instrument show more promise. The values are only about 4 to 6 times higher than those from the VGF KL-1 bridge or with the Gouy balance, instead of 10 to 20 times for the powder form charcoals.

(4) The BPL charcoal and DREO-11 both have the lowest susceptibility values, this couples with the observations that the commercial ASC-whetlerites have higher susceptibilities than the custom-made charcoals, and is consistent with the Gouy balance results. However, the magnetic susceptibility results for the custom-made charcoals do not represent a good fit in a multiple linear regression model. This is due to the fact that the differences in the magnetic susceptibility values are too small in this order of magnitude.

In conclusion, it seems that the commercial susceptometers yield reasonable qualitative assessment of the magnetic susceptibilities of the impregnated charcoals in some cases. However for the whole series of observations, these two commercial instruments fail to show the trends of the two kinds of charcoals and the linearity of the magnetic susceptibility with respect to the concentrations of the impregnants.

However, it should be noted that the time saved using these commercial instruments is tremendous. For example, the charcoal after impregnation is in the pellet form, it can be immediately transferred to a vial and the magnetic susceptibility measured. Using the Gouy balance, the

charcoal sample has to be ground and dried, and then transferred to a 5 mm o.d. tube before measurement. The magnet and the balance have to be calibrated in the mean time. Then a series of measurements have to be taken from 1.0 to 7.5 kG, and so on. This is obviously a very long and laborous job.

From the present results, these two commercial instruments obviously are not suitable for this charcoal study but it certainly does not rule out the possibilities of the use of other commercial susceptometers. It is anticipated that this report will lay down some preliminary ground work and direction for future study in this area of charcoal research.

TABLE A-1

Table A-1 Magnetic Susceptibilities of ASC-Whetlerites Measured by Commercial Instruments

Charcoal	VGF - KL 1		Sapphire Instruments	
	Powder Form	Pellet Form	Powder Form	Pellet Form
	K x 10^{-6} (emu-ml^{-1})		K x 10^{-6} (emu-ml^{-1})	
BPL	10.50	15.28	181.3	66.25
CAL-1034	26.64	30.40	140.6	109.2
CAL-1275	21.41	29.34	257.2	101.2
CAL-1048	22.79	21.65	112.4	80.92
DREO-01	17.94	16.83	91.59	68.13
DREO-02	10.21	18.90	110.9	70.58
DREO-03	13.97	19.42	241.5	72.43
DREO-04	13.89	19.58	238.8	69.56
DREO-05	20.49	21.29	96.38	73.00
DREO-06	10.07	18.14	77.97	72.17
DREO-07	21.29	19.89	95.16	73.29
DREO-08	22.56	20.89	99.13	74.88
DREO-09	18.74	21.09	92.40	72.81
	ASC Whetlerites Co-Impregnated with TEDA			
CAL-1.5	16.39		91.59	
CAL-3	22.92		105.9	
CAL-6	14.77		263.0	
CAL-10	16.00		280.6	
DREO-10	18.78	20.69	96.28	73.24
DREO-11	18.30	15.32	81.40	66.87
DREO-12	11.13	19.50	126.7	72.41

APPENDIX B

IMPURITIES IN THE CHARCOAL

As was pointed out in section 4.3, the volume susceptibility of the base charcoal (BPL) is not equal to zero. The explanation was that this may be due to the presence of ferromagnetic impurities or ash. To account for this, neutron activation analysis for 55 elements was performed on two charcoal samples, namely the BPL and the CAL-1048, both supplied directly from Calgon Carbon Corporation. The result of the analysis is summarized in Tables B-1 and B-2.

From data in Table B-1, the main ferromagnetic impurity in the BPL charcoal is iron, which is about 0.5%. The other impurities, except nickel (which is also ferromagnetic), are lower in concentration and all have small or negligible magnetic susceptibilities. Therefore the residual magnetic susceptibility on the charcoal could be attributed to the presence of iron, in its elemental form or oxidized form.

From Table B-2, the content of iron on CAL-1048 is the same as that of the BPL-charcoal. This probably indicates that the concentrations of iron do not vary among samples and with different preparations (i.e. from base charcoal to impregnated charcoal). The contents of the other impurities vary slightly (from those on the base charcoal) due to the attenuation or enhancement of signal because of the large concentration of copper and chromium. For CAL-1048, a drastic increase in the amount of copper, chromium and silver compared to BPL is observed due to the added impregnants. The concentration of chromium and silver is very close to the values obtained by analysis performed in this laboratory. There is some variation in the copper concentration obtained, but this could be attributed to differences in sampling, as the copper conglomerates into crystallites of Cu_2O upon aging. The other reason for the low value of copper could be due to the interference from the long-life radioactive chromium species in the neutron activation analysis.

As the concentration of the major impurity (iron, in this case) does not vary significantly between these two samples, it may be assumed that:

(1) all charcoals used in this report have the same residual magnetic susceptibility (given by the value of about 10 $emu\text{-}ml^{-1}$ on the BPL charcoal); and

(2) the contributions of the other paramagnetic species (added as impregnants) to the bulk magnetic susceptibility act as simple additional constituents.

These two conjectures are important factors in this study, and they seem to hold from these experimental results.

TABLE B-1

Result of Neutron Activation Analysis on the
BPL-Charcoal (Coal-Based, no impregnants)

Element	Content	RSD,%	Element	Content	RSD,%
Aluminum (%)	1.10	3.6	Silicon (%)	< 2.50	
Antimony	3.32	3.9	Silver	< 2.80	
Arsenic	14.3	4.1	Sodium (%)	6.750E-02	4.0
Barium	108.0	9.5	Strontium	210	13.1
Bromine	1.50	15.3	Sulphur (%)	2.60	
Cadmium	< 2.70		Tantalum	0.120	35.8
Calcium (%)	0.130	18.9	Tellurium	< 6.60	
Cesium	<0.740		Thorium	1.80	9.9
Chlorine	75.0	12.1	Tin	< 280	
Chromium	17.0	11.7	Titanium (%)	6.730E-02	8.8
Cobalt	17.5	4.2	Tungsten	1.60	30.1
Copper	56.0	36.4	Uranium	1.60	10.5
Gallium	< 6.70		Vanadium	47.4	4.2
Germanium	< 67.0		Zinc	< 18.0	
Gold (PPB)	< 3.10		Zirconium	< 220	
Hafnium	0.690	31.0			
Indium	<2.100E-02		Rare Earths:		
Iodine	3.20	12.0			
Iridium (PPB)	<10.0		Cerium	29.1	5.1
Iron (%)	0.487	5.4	Dysprosium	3.22	4.7
Magnesium (%)	<8.200E-02		Europium	0.557	5.3
Manganese	9.52	8.7	Holmium	0.776	9.6
Molybdenum	3.60	17.8	Lanthanum	14.3	3.8
Nickel	< 370		Lutetium	0.170	21.9
Niobim	< 340		Neodymium	18.0	11.0
Potassium (%)	6.100E-02	28.3	Praseodymium	< 13.0	
Rhenium	<1.400E-02		Samarium	2.69	3.0
Rubidium	<16.0		Terbium	<0.400	
Scandium	5.10	3.4	Thulium	<0.260	
Selenium	3.40	23.3	Ytterbium	1.13	7.1

NOTES: - Results in Micrograms per gram dry weight (except as noted).
- RSD = Relative Standard Deviation (1 sigma) in per cent.
- Extra significant figures are quoted. Round results in accordance with our estimate of the individual RSD.

TABLE B-2

Result of Neutron Activation Analysis on the Charcoal CAL-1048 (Calgon ASC Whetlerite)

Element	Content	RSD,%	Element	Content	RSD,%
Aluminum (%)	1.21	4.5	Silicon (%)	< 12.0	
Antimony	2.80	4.5	Silver	< 356	3.5
Arsenic	15.8	4.2	Sodium (%)	6.010E-02	4.0
Barium	<220.0		Strontium	< 380	
Bromine	1.60	18.2	Sulphur (%)	< 3.00	
Cadmium	< 8.20		Tantalum	< 0.460	24.3
Calcium (%)	9.300E-02	37.5	Tellurium	< 26.0	
Cesium	< 1.20		Thorium	11.5	6.9
Chlorine	46.0	34.7	Tin	< 580	
Chromium	2.300E+04	3.0	Titanium (%)	0.100	
Cobalt	13.9	5.5	Tungsten	4.40	15.6
Copper	4.900E+04	3.1	Uranium	1.30	44.9
Gallium	< 50.0		Vanadium	54.4	6.9
Germanium	< 500		Zinc	< 47.0	
Gold (PPB)	< 5.70		Zirconium	< 360	
Hafnium	<0.940				
Indium	<9.100E-02		Rare Earths:		
Iodine	4.50				
Iridium (PPB)	<24.0		Cerium	95.0	6.6
Iron (%)	0.463	7.6	Dysprosium	2.20	23.6
Magnesium (%)	<0.340		Europium	0.340	27.2
Manganese	13.0	13.5	Holmium	<0.370	
Molybdenum	26.0	14.6	Lanthanum	10.1	6.6
Nickel	< 720		Lutetium	<0.280	
Niobim	<2.200E+03		Neodymium	< 18.0	
Potassium (%)	0.120	17.6	Praseodymium	< 13.0	
Rhenium	<5.300E-02		Samarium	1.91	3.2
Rubidium	<32.0		Terbium	<0.650	
Scandium	4.34	3.8	Thulium	<0.890	
Selenium	8.90		Ytterbium	1.00	12.5

NOTES: - Results in micrograms per gram dry weight (except as noted).
- RSD = Relative Standard Deviation (1 sigma) in per cent.
- Extra significant figures are quoted. Round results in accordance with our estimate of the individual RSD.

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A non-destructive test has been developed to monitor the impregnants in charcoal. A study of some commercially-produced and custom-made ASC-whetlerites indicates significant increases in the measured magnetic susceptibility from that of the base charcoal. Correlations between the measured susceptibilities and the concentrations of copper and chromium by a linear mathematical model are established with reasonably good fit for the custom-made charcoals. It is concluded that the magnetic susceptibility data would be best utilized as a qualitative tool for the assessment of metal impregnants on charcoal, rather than for precise quantitative analyses. Some preliminary data on the magnetic susceptibilities of ASC-whetlerites co-impregnated with TEDA are also presented. Magnetic susceptibilities measured on the same charcoal samples by commercial instruments indicate that although they show similar trends as the Gouy balance, these instruments are subject to too much variation to be of any qualitative and/or quantitative use for ASC charcoals.

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